PCT/AU2004/000428

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for making aluminosilicates of zeolite N structure comprising the steps of:
   (i) combining a water soluble monovalent cation, a solution of hydroxyl anions and an aluminosilicate to form a resultant mixture having a pH greater than 10 and a H_2O/Al_2O_3 ratio in the range 30 to 220;
   (ii) heating the resultant mixture to a temperature of between 50°C and the boiling point of the mixture for a time between 1 minute and 100 hours until a crystalline product of zeolite N structure is formed as determined by X-ray diffraction or other suitable characteristic; and
   (iii) separating the zeolite N product as a solid from the mixture.
2. A process as claimed in claim 1 wherein the water soluble monovalent cation in step (i) is an alkali metal or an ammonium ion or mixtures of these ions.
3. A process as claimed in claim 2 wherein the alkali metal comprises a potassium ion.
4. A process as claimed in claim 2 wherein the alkali metal comprises a sodium ion.
5. A process as claimed in claim 2 wherein the alkali metal comprises both a potassium and sodium ion.
6. A process as claimed in claim 2 wherein the monovalent cation comprises both potassium and ammonium ions.
7. A process as claimed in any preceding claim wherein the resultant mixture of step (i) also contains a halide.
8. A process as claimed in claim 7 wherein the halide is chloride.
9. A process as claimed in any preceding claim wherein the pH of the solution of hydroxyl ions is greater than 13.
10. A process as claimed in any preceding claim wherein in step (ii) the resultant mixture is heated to a temperature of in the range 80°C to 95°C.
11. A process as claimed in any preceding claim wherein the aluminosilicate has a Si:Al ratio in the range 1.0 to 5.0.
12. A process as claimed in claim 11 wherein the aluminosilicate has a Si:Al ratio in the range 1.0 to 3.0.
13. A process as claimed in claim 11 wherein the aluminosilicate is a clay.
14. A process as claimed in claim 13 wherein the clay is kaolin or montmorillonite or mixtures thereof.
15. A process as claimed in any preceding claim wherein in step (ii) said heating is carried out for a time in the range 2 to 24 hours.
16. A process as claimed in any preceding claim wherein the ratio of H_2O/Al_2O_3 in the mixture of step (i) is in the range 45 to 65.
17. A process as claimed in any preceding claim wherein in step (i) a quantity of solid zeolite N is added to the mixture.

PCT/AU2004/000428

18. A process as claimed in any preceding claim wherein caustic liquor remaining in the mixture after step (iii) is re-used as at least part of a solution of anions in step (i) for subsequent production of additional zeolite N product.

19. A process as claimed in claim 3 wherein the amount of potassium utilised is governed by a ratio of K_2O/Al_20_3 in the range 0.3 to 15.

20. A process as claimed in claim 3 wherein the amount of potassium utilised is governed by a ratio of KCl/Al_20_3 in the range 0.0 to 15.

21. A process as claimed in claim 8 wherein the amount of chloride utilised is governed by a ratio of KCl/Al_20_3 in the range 0.0 to 15.

22. A process as claimed in claim 4 wherein the amount of sodium utilised is governed by a ratio of Na_2O / Al_2O_3 in the range 0.0 to 2.5.

23. A process as claimed in claim 4 wherein the amount of sodium utilised is governed by a ratio of NaCl / Al_2O_3 in the range 0.0 to 2.8.

24. A process as claimed in claim 8 wherein the amount of chloride utilised is governed by a ratio of NaCl / Al_2O_3 in the range 0.0 to 2.8.

25. A process as claimed in claim 8 wherein the amount of chloride utilised is governed by a ratio of Cl / SiO_2 in the range 0.0 to 6.5.

26. A process as claimed in claim 5 wherein the amount of sodium and potassium utilised is governed by a ratio of K/(K+Na) in the range 0.5 to 1.0.

27. A process as claimed in claim 5 wherein the amount of sodium and potassium utilised is governed by a ratio of (K + Na – Al)/ Si ratio in the range 2.0 to 18.0.

29. Zeolite N produced by the process of any preceding claim or combination of preceding claims.

30. Zeolite N produced by the process of any preceding claim having a composition according to the formula

$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cation(s) exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \leq a \leq 1,\ 1 \leq c/b \leq \infty,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$.

31. Zeolite N having a composition according to the formula

$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \leq a \leq 1,\ 1 \leq c/b \leq \infty,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$

with the proviso that when a = 0, b = 1, c = 1, d = 0, X = Cl, M $\neq$ K.

PCT/AU2004/000428

32. Zeolite N having a composition according to the formula $(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$
characterised in having a BET surface area greater than 1 m^2/g.
33. Zeolite N as claimed in claim 32 having a BET surface area between 1 m^2/g and 150 m^2/g.
34. Zeolite N as claimed in claim 33 having a BET surface area between 5 m^2/g and 150 m^2/g.
35. Zeolite N as claimed in any one of claims 32, 33 or 34 having a proportion of external surface area to internal surface area of greater than 1%.
36. Zeolite N as claimed in claim 35 having a proportion of external surface area to internal surface area of greater than 5%.
37. Zeolite N as claimed in claim 36 having a proportion of external surface area to internal surface area of greater than 10%.
38. Zeolite N having a composition according to the formula $(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$
characterised in having an X-ray diffraction pattern which has a high background intensity of greater than 5% of a maximum peak height between the region $25° < 2\theta < 70°$.
39. Zeolite N having a composition according to the formula $(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$
when used for exchange of ammonium ions in solution.
40. Zeolite N having a composition according to the formula $(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

PCT/AU2004/000428

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \le a \le 1$, $1 \le c/b \le \infty$, $0 \le d \le 1$ and $1 \le n \le 10$.

when used for exchange of ammonium ions in the presence of alkali metal and/or alkaline earth metal ions in solution.

41. Zeolite N having a composition according to the formula $(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \le a \le 1$, $1 \le c/b \le \infty$, $0 \le d \le 1$ and $1 \le n \le 10$.

having a cation exchange capacity ranging from 100 meq per 100g to 700 meq per 100g for ammonium ions with concentrations between less than 1 mg/L to greater than 10,000 mg/L.

42. Zeolite N as claimed in claim 41 having a cation exchange capacity greater than 200 meq per 100g.

43. Zeolite N having a composition according to the formula $(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \le a \le 1$, $1 \le c/b \le \infty$, $0 \le d \le 1$ and $1 \le n \le 10$

when used for exchange of metal ions in solution.

44. Zeolite N having a composition according to the formula $(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \le a \le 1$, $1 \le c/b \le \infty$, $0 \le d \le 1$ and $1 \le n \le 10$

when used for exchange of metal ions in the presence of alkali metal or alkaline earth metal ions in solution.

45. Zeolite N as claimed in claim 43 or 44 wherein the metal ions comprise copper, zinc, nickel, cobalt, cadmium, silver and lead.

PCT/AU2004/000428

46. Zeolite N as claimed in claim 43, 44 or 45 having cation exchange capacity for metal ions ranging from 20meq per 100g to 400meq per 100g.

47. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \le a \le 1,\ 1 \le c/b \le \infty,\ 0 \le d \le 1$ and $1 \le n \le 10$
when used for adsorbing ammonia gas in the temperature range 0°C to 300°C.

48. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \le a \le 1,\ 1 \le c/b \le \infty,\ 0 \le d \le 1$ and $1 \le n \le 10$
when used for adsorbing ammonia gas in the temperature range 0°C to 300°C in the presence of water.

49. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \le a \le 1,\ 1 \le c/b \le \infty,\ 0 \le d \le 1$ and $1 \le n \le 10$
when used for absorbing oil.

50. Zeolite N as claimed in claim 49 when used for absorbing oil greater than 50g of oil per 100g of Zeolite N.

51. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \le a \le 1,\ 1 \le c/b \le \infty,\ 0 \le d \le 1$ and $1 \le n \le 10$
when used for removing anions from wastewater.

52. Zeolite N having a composition according to the formula

PCT/AU2004/000428

$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$

when used in an ammonium form to have a capacity to re-exchange alkali metal ions from solutions containing hydroxyl ions ranging in concentration from 0.1 M to 2.0M.

53. Zeolite N as claimed in claim 52 wherein the concentration of hydroxyl ions is from 0.4 M to 1.5 M.

54. Zeolite N as claimed in claim 52 or 53 wherein the solutions containing hydroxyl ions comprise KOH or NaOH or mixtures thereof.

55. Zeolite N having a composition according to the formula

$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$

having a removal rate of ammonium ion ranging between 50-100% from ammonium loaded Zeolite N using a regeneration solution containing hydroxyl ions.

56. Zeolite N having a composition according to the formula

$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$

when used to re-exchange ammonium ions and/or to retain high selectivity for ammonium ions after regeneration with a solution containing hydroxyl ions.

57. Zeolite N having a composition according to the formula

$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$

PCT/AU2004/000428

when used to kill gram positive or gram negative bacteria.

58. Zeolite N having a composition according to the formula $(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = potassium or sodium or ammonium;

P = silver or zinc

X = halide and Y is an anion and

$0 \leq a \leq 1,\ 1 \leq c/b \leq \propto,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$

when used to kill gram positive or gram negative bacteria.

59. Zeolite N having a composition according to the formula $(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = potassium and ammonium;

P = silver and zinc

X = halide and Y is an anion and

$0 \leq a \leq 1,\ 1 \leq c/b \leq \propto,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$

when used to kill gram positive or gram negative bacteria.

60. Zeolite N having a composition according to the formula $(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \leq a \leq 1,\ 1 \leq c/b \leq \propto,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$.

where c/b is greater than 1.

61. Zeolite N as claimed in claim 60 wherein c/b has an upper value of 5.

62. Zeolite N as claimed in claim 60 wherein c/b has an upper value of 3.

63. Zeolite N as claimed in any one of claims 30-62 wherein Y is hydroxyl or halide.

64. Zeolite N as claimed in claim 63 wherein Y is chloride.

PCT/AU2004/000428

Bibliography

Acara, N.A., US Patent 3,414,602, December 3rd, 1968.

Baerlocher, Ch. and R. M. Barrer, *Z. Kristallogr.*, **140**, 10-26, 1974.

Baerlocher, Ch., and W.M. Meier, *Z. Kristallogr.*, **135**, 339-354, 1972.

Barrer, R.M. and J.W. Baynham, *J. Chem. Soc.*, 2882-2891, 1956.

Barrer, R.M., K. Bromley and P.J. Denny, US Patent 3,306,922, February 28th, 1967.

Barrer, R.M., L. Hinds and E.A. White, *J. Chem Soc.*, 1466-1475, 1953.

Barrer, R.M. and C. Marcilly, *J. Chem. Soc. (A)*, 2735-2745, 1970.

Barrer, R.M. and B.M. Munday, *J. Chem. Soc. (A)*, 2914-2920, 1971.

Breck, D.W. "Zeolite Molecular Sieves: structure, chemistry and use", John Wiley and Sons, New York, 771pp, 1974.

Breck, D.W. US Patent 3,723,308, March 27th, 1973.

Christensen, A. Norlund and H. Fjellvag, *Acta Chemica Scandinavica*, **51**, 969-973, 1997.

Christensen, A. Norlund and H. Fjellvag, *Acta Chemica Scandinavica*, **53**, 85-89, 1999.

Jaynes, W.F. and J.M. Bigham, *Clays and Clay Minerals*, **34**, 93-98, 1986.

Komarowski, S. and Q. Yu, *Environmental Tech.*, **18**, 1085-1097, 1997.

Mackinnon, I.D.R., D. Page and B. Singh, US Patent 6,218,329B1, March 13th, 2001.

Mackinnon, I.D.R., D. Page and B. Singh, US Patent 6,218,329B2, April 17th, 2001.

Sherman, J.D. In *Molecular Sieves II* (J.R. Katzer, *ed.*) ACS Symposium Series, 30-42, American Chemical Society, Washington DC., 1977.

Sherman, J.D. and R.J. Ross, US Patent 4,344,851, August 17th, 1982.

PCT/AU2004/000428

Szostak, R., Molecular Sieves. Principles of Synthesis and Identification. Blackie Academic and Professional, 2nd edition, 359pp. 1998.

Thompson, J.G., I.D.R. Mackinnon, S. Koun and N. Gabbitas, US Patent 5,858,081, January 12th, 1999.

Van Olphen, H., and J.J. Fripiat (eds) Data Handbook for Clay Materials and other Non-metallic Minerals, Pergamon Press, 346pp., 1979.

Weitkamp, J. and L. Puppe (Eds.), Catalysis and Zeolites: Fundamentals and Applications, Springer-Verlag, Berlin, 1999.